

Ecological risk assessment and spatial distribution of heavy metals in surface sediments. A case study of two small storage reservoirs, SE Poland

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ABSTRACT

The article shows the results of research on heavy metals (Cr, Zn, Ni, Cu, Pb, Cd) content in bottom sediments of two small storage reservoirs located in the south-eastern part of Poland. The analyses covered the top 10 cm layer of sediment samples taken in transects perpendicular to the shoreline, located in upper, central and lower sections of the studied reservoirs. The ordinary kriging method was applied to interpolate spatial distribution of heavy metals content in the sediments. The assessment of surface sediment contamination with heavy metals was based on a threshold effect level and probable effect level methods. In addition, the ecological risk was assessed on the basis of the indices: potential ecological risk index and toxic risk index. Moreover, the principal component analysis was carried out to find determinants for the distribution of the analyzed trace elements in reservoirs. The results of the completed analysis have proven that the highest concentrations of heavy metals (HM) are found in the vicinity of dams in both reservoirs. Calculated probable effects level values indicate a negative impact of Pb- Bliżyn Reservoir (BR) and Cd- Małoszówka Reservoir (MR) on aquatic biota. The analysis of heavy metal content and their interrelationships in surface sediments proves that Pb, Cu and Zn in the BR and Cd and Cr in the MR have anthropogenic origins. Moreover, the main determinants for HM distribution in the reservoir are hydromorphological parameters, which determine sediment grading and organic matter transport.

Keywords: Small water reservoir; Surface sediments; Pollution; Heavy metals; Spatial distribution; Ecological risk

1. Introduction

Water reservoirs have an important function in the provision of water resources and circulation of matter within a certain area. They preserve and enrich species diversity, constitute an important landscaping element, store water needed for proper activity of industry and satisfy the demands of people. Water reservoirs also affect riverine hydrological regimes and sediment transportation. Different organic and inorganic pollutants, including heavy metals (HMs) [1–5], are retained together with the reservoir-deposited sediments. HMs retained with sediments in water reservoirs may originate both from natural (e.g. rock and soil weathering) and anthropogenic sources (e.g. industrial, municipal and agricultural effluents) [67]. In the aquatic environment, HMs constitute a serious threat due to their toxicity, persistence (they are not biodegradable), and

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ability to accumulate in sediments and living organisms (plants, animals), even if delivered in a small volume and seasonally [8–11].

Many different factors affect HMs content and distribution in a reservoir. These factors can be divided into hydrological, geomorphological, hydrodynamic, and operating. The volume of water and sediments entering a reservoir, as well as its composition and chemical properties, depend on river hydrological regime and anthropogenic activity [12]. Generally, the highest concentrations of HMs are found in bottom sediments in the vicinity of strongly polluted tributaries and near dams, where fine-grained material is deposited. Fine-grained sediments contain higher HMs concentrations as a result higher magnetic susceptibility [13]. Therefore, many researchers point at direct relations between the spatial distribution of HMs and sediments granulation, and organic matter content [14-17]. In shallow reservoirs, HMs bound to sediments may undergo redistribution due to water movements caused by undulation. Due to the resuspension processes, they also may be the source of secondary contamination in water depths [1].

The chemical analysis of bottom sediments provides a lot of useful data on reservoir pollution. The assessment of the chemical quality of sediments is of key importance for the development of strategies for sediment management purposes [18]. As a result, current research into trace elements in bottom sediments includes environmental risk, geochemical cycle, and toxicity assessment. Ecological risk index (PERI) and toxic risk index (TRI) are among the group of methods that allow quantitative assessment of cumulative aquatic environment pollution with HMs [19]. The assessment of sediment quality with respect to HM pollution is also made based on ecotoxicological criteria like threshold effects level (TEL), and probable effects level (PEL).

In spite of many results of studies available now, there are still some deficiencies, which need to be recognized. Considering this, the main purposes of this publication are: (i) the analysis of HMs concentrations and distribution in bottom sediments of the studied reservoirs, (ii) ecological risk assessment, and (iii) identification of factors determining the spatial distribution of HMs in the reservoir.

2. Study area

The scope of the research covered two small water reservoirs located in south-eastern Poland in Świętokrzyskie Voivodeship Fig. 1. They close catchments characterized by diverse land development (Table 1). Forests prevail in (BR) catchment, occupying 69% of a total catchment area, while farmland dominates in (MR) catchment (88% of total catchment area). In the BR catchment, there are many coal storages and building material warehouses, as well as a paint and lacquer production plant. Moreover, along with left shore of the reservoir, there are numerous stormwater drainage discharges, which deliver stormwater from transportation routes and built-up areas in Bliżyn village. The MR catchment is a typically agricultural area, where corn and vegetables are grown in its fertile soils-the largest areas are covered by wheat and barley crops. Moreover, swine are bred in local farms on an industrial scale. In both catchments, built-up areas concentrate along transportation routes.

Table 1 Basic characteristics of the studied reservoirs and catchments

Parameter	Bliżyn	Małoszówka						
	Reservoir	Reservoir						
Catchment characteristics								
Catchment area-CA (km ²)	83	102						
Forests–F (%)	69	2						
Agricultural areas–AA (%)	23	88						
Built-up areas–U (%)	1.5	2.8						
Meadows/wastelands-M (%)	6.5	7.2						
Mean catchment slope–J (%)	1.6	1.3						
River network density-RD	0.56	0.66						
(km km ⁻²)								
Road network density –DR	0.54	0.96						
(km km ⁻²)								
H _{min} (m asl)	256.50	192.00						
H _{max} (m asl)	408.00	332.40						
Reservoir characteristics								
Construction year	2011	2013						
Capacity–V (thousands m ³)	182	400						
Water table area–RA (ha)	10.34	20.93						
Mean depth–MD (m)	1.76	1.91						
Maximum depth–MaxD (m)	4.4	4.5						
Retention time-RT (h)	340	607						

The analyzed reservoirs are characterized by small capacity (182,000–400,000 m³) and flooding area (10–21 ha). They are shallow reservoirs, in which mean depth does not exceed 2.0 m. The maximum depth of both reservoirs ranges within 4.5 m near the dams. The BR is characterized by oblong shape and maximum width 150 m, while MR is rather triangular-shaped, with maximum width in the vicinity of the dam reaching 400 m.

3. Materials and methods

3.1. Sediment sampling

The samples of bottom sediments from the analyzed reservoirs were taken in 2018 from the top 10 cm layer using Becker type sampler. In total, 29 sediment samples were taken from both reservoirs (14 from the BR and 15 from the MR). Sediment sample taking locations shown in Fig. 1 were determined using a GPS receiver.

3.2. Sample preparation and analysis

Bottom sediment samples were analyzed in order to determine the following parameters: total concentration of trace elements HM, grain composition, and total organic matter (TOM). The samples for the determination of HM (Cr, Zn, Ni, Cu, Pb, Cd) concentrations were dried at the temperature of 105°C until a constant mass was obtained and then ground in a porcelain mortar. Weighed 0.2 g samples were put in Teflon receptacles, then concentrated nitric



Fig. 1. Location of studied reservoirs.

acid (V) was added, and the samples were put to microwave mineralization in a Multiwave 3,000 oven from Anton Paar, Graz, Austria. The HM content was determined using optical emission spectrometry with inductively coupled plasma ICP-OES Optima 8,000 (Perkin Elmer, Waltham, MA, USA) against multi-element patterns [20]. TOM was measured by the Tyurin method with wet oxidation, followed by ferrous ammonium sulphate titration [21].

Grain composition of bottom sediments was determined using the laser diffraction method with a Mastersizer 3,000 instrument (from Malvern Instruments, Malvern, UK) with a particle size range of $0.20-3,000.00 \ \mu m$.

3.3. Ecological risk assessment

Ecological risk assessment was carried out on the basis of the PERI proposed by Hakanson [22] and TRI developed by Zhang et al. [23]. The PERI index consists of three basic modules: the degree of contamination (C_D), toxic-response factor (T_r) and potential ecological risk factor (E_r). According to this method, PERI can be calculated using the following formula [22–24]:

$$\text{PERI} = \sum_{1}^{n} E_{r}^{i} = \sum_{1}^{n} T_{r}^{i} C_{f}^{i} = \sum_{1}^{n} T_{r}^{i} \frac{C_{D}^{i}}{C_{B}^{i}} \tag{1}$$

where E_r^i is the potential risk of individual heavy metal, T_r^i is the toxic-response factor of the trace elements, C_f^i is the contamination factor for the individual metal, C_D^i is the present concentration of the trace elements in the sediments, and C_B^i is the background value of the trace elements in the study area

The toxic-response factor of the trace elements depends on sedimentological toxic factor (STF) and bioproduction index (BPI), and it can be calculated for each HMs as follows: Cr = $2 \cdot (5/BPI)^{1/2}$, Zn = $1 \cdot (5/BPI)^{1/2}$, Ni = $5 \cdot (5/BPI)^{1/2}$, Cu = $5 \cdot (5/BPI)^{1/2}$, Pb = $5 \cdot (5/BPI)^{1/2}$, Cd = $30 \cdot (5/BPI)^{1/2}$. The BPI was calculated as the nitrogen content in the regression line for organic matter content of 10%. The value of BPI was equal to 35.4 and 43.2, respectively, for Bliżyn and Małoszówka Reservoir. The contamination factor (C_{j}^{2}) for individual heavy metals was calculated as the ratio of trace element content in a sediment sample (C_{D}^{1}) to geochemical background (C_{B}^{1}) , which was [25]: for Cr - 5 mg kg⁻¹, Zn - 48 mg kg⁻¹, Ni - 5 mg kg⁻¹, Cu - 6 mg kg⁻¹, Pb - 10 mg kg⁻¹, and Cd - 0.5 mg kg⁻¹.

The TRI index is based on the TEL specifying upper limit of pollutant concentration range, below which adverse effect on the aquatic organisms occurs quite rarely, and PEL (Table 2) defined as lower limit of pollutant concentrations, which may have significant adverse effect on living organisms [26], and can be calculated using the formula [13]:

$$\text{TRI} = \sum_{i=1}^{n} \text{TRI}_{i} = \sum_{i=1}^{n} \sqrt{\frac{\left(\frac{C_{i}}{\text{TEL}}\right)^{2} + \left(\frac{C_{i}}{\text{PEL}}\right)^{2}}{2}}$$
(2)

where C_i is the content of each heavy metal in the sediment sample, and TRI_i is the toxic risk index of individual heavy metal.

3.4. Statistical analysis

Obtained values of bottom sediment pollution indices were characterized using an arithmetic mean, standard deviation, minimum and maximum value, and coefficient of variation (CV). The normality of data was checked by the Kolmogorov–Smirnov (K–S) test. Box-Cox transformation

PERI-value ^a		Grades of potential e risk of the environme	ecological ent	TR	I-value ^b	e ^b Grades of potential ecological risk of the environment				
<150		Low ecological risk		≤5			No toxic risk			
$150 \leq \mathrm{PERI} < 300$		Moderate ecological	risk	5 <	$\text{TRI} \le 10$		Low toxic risk			
$300 \le \text{PERI} < 600$		Considerable ecolog	ical risk	10	< TRI ≤ 15		Moderate toxic risk			
$PERI \ge 600$		Very high ecological	risk	15	< TRI ≤ 20	$RI \le 20$ Considerable toxic risk				
				TRI > 20 Very high toxic risk			ery high toxic risk			
Sediment quality guidelines (mg kg ⁻¹)										
	Cr	Zn	Ni		Cu		Pb	Cd		
PEL ^c	90.0	315	36		197.0		91.3	3.530		
TEL^{c}	37.3	123	18		35.7		35.0	0.596		

Note: ^{*a*} – acc. to [22]; ^{*b*} – acc. to [13]; ^{*c*} – acc. to [26].

was applied to normalize abnormal data. Pearson correlation coefficient was calculated in order to determine the strength and direction of statistical relations between the analyzed variables (the level $p \le 0.05$ was deemed statistically significant). Identification of factors determining the spatial distribution of the analyzed HMs content in bottom sediments was carried out on the basis of the results of principal component analysis (PCA) analysis. The analysis covered the following factors affecting spatial distribution of HMs: grain composition of sediments (percentage of silt (Cl, $d_i < 0.002$ mm), dust (Si, $0.002 \le d_i < 0.063$ mm) and sand (Sa, $0.063 \le d_i < 2.0$ mm)), TOM, and the distance between sampling site location and reservoir inlet (LI) and outlet (LO). Statistical analysis were performed using the Statistica 8.0 software.

3.5. Spatial interpolation methodology

The ordinary kriging (OK) method was used for interpolation purposes (to create a regular network of values). The OK belongs to statistical interpolation methods and involves the estimation of values in a given point on the basis of measurement data obtained near this point (in its vicinity). Whereas, it is assumed that the degree of interaction among dispersed points depends on the distance between them. The structure of dependence between the mean diversity of HM concentration values (semi-variance) and the distances among measuring points is characterized by variogram [27]. For regular measuring network the value of semi-variance ($\gamma_{(1)}$) is determined using Eq. (3), while the value in the interpolation point is calculated as a weighted mean, using Eq. (4)[1].

$$\gamma_{(l)} = \frac{\sum_{i=1}^{n} \left[HM(x) - HM(x+l) \right]^{2}}{2n}$$
(3)

where HM(x), HM(x+1) – total concentration of trace element in measuring points distant by value *l*, *n* is the number of pairs of measuring points distant by value *l*.

$$\operatorname{HM}(x_0)^* = \sum_{i=1}^n w_i \operatorname{HM}(x_i)$$
(4)

where w_i is the weighting factors, $HM(x_0)^*$ is the total concentration of trace element in the interpolated point, $HM(x_i)$ is the total concentration of trace elements in the measuring point.

The spatial distribution of HM in the sediment samples of studied reservoirs was carried using OK model in Surfer 11 program.

4. Results and discussion

4.1. Heavy metal concentration and physical properties of bottom sediments

The fine-grained material with prevailing sand and dust fractions is firstly retained in the analyzed reservoirs. At the same time, grains with a diameter under 2 μ m are almost entirely carried beyond the studied reservoirs. The content of silt fraction grains did not exceed 3.5% of the total mass of the analyzed sediment samples (Table 3). This value corresponds to the results of studies on the grain composition of sediments in small reservoirs within Poland [1,28]. In the MR, grains of the sand fraction was deposited primarily in the upper part of the reservoir, while dust sediments prevailed in the middle and near-dam areas Fig. 2. The maximum content of dust fraction grains (Si > 95%) was observed in the samples taken in the vicinity of the reservoir dam. It was different in the case of the BR. Besides the upper part of the reservoir, sediments with significant sand fraction content also appeared along its northern shore with stormwater drainage discharges (Sa > 25%). Along with stormwater, considerable suspension volumes enter the reservoir, changing the natural composition of sediments. The TOM content in sediments ranged from 0.30 to 12.80% in the BR, and from 3.90% to 16.20% in the MR Fig. 2. Obtained TOM values comply with those specified by [1,29-31] for small retention reservoirs. While analyzing percent spatial distribution of TOM in sediments, it can be observed that

Table 3 HM concentration in bottom sediments

Parameters	Cr	Zn	Ni	Cu	Pb	Cd	Cl	Si	Sa	TOM
			Mg	kg ⁻¹				%		
Bliżyn Reservoir										
Maximum	14.89	201.87	31.15	45.50	110.20	0.57	2.00	81.00	92.00	12.80
Minimum	6.06	36.60	5.80	9.36	30.61	0.11	0.00	8.00	18.00	0.30
Mean	10.65	122.55	19.47	20.00	62.53	0.34	1.00	57.57	41.43	7.15
Median	12.49	123.70	19.08	15.36	45.23	0.33	1.25	67.25	31.50	7.95
CV %	35	45	49	57	45	44	76	46	65	61
Małoszówka Reservoir										
Maximum	23.51	94.78	6.80	20.95	20.75	11.50	3.50	95.50	95.00	16.20
Minimum	7.22	55.30	2.40	14.18	5.01	5.71	0.00	5.50	1.00	3.90
Mean	13.71	78.02	4.53	17.01	13.97	8.81	1.77	60.39	37.84	8.54
Median	13.50	83.07	4.25	17.04	13.88	9.14	2.00	65.50	32.50	8.60
CV %	33	17	24	11	32	17	69	45	74	34



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40 60 80



Fig. 2. Spatial distribution of grain size and TOM.

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there is a clear division into sediments, in which the share of TOM ranges from few to more than ten percent – these are fine-grained sediments taken from central and near-dam part of the reservoir, where driving force of water stream is insignificant. At the same time, sand sediments accumulated directly at the inlet prove to have TOM share under 2%. This is justified by the greater driving force of the water stream, as a result of which organic matter is transported further into the reservoir [1,12].

The mean content of trace elements in the top layer of sediments from the BR and MR can be sequenced as follows: Zn > Pb > Cu > Mi > Cr > Cd and Zn > Cu > Pb > Cr > Cd > Ni, respectively. The highest concentration of Zn (201.87 mg kg⁻¹), Cu (45.50 mg kg⁻¹) and Pb (111.20 mg kg⁻¹) was observed in sediment samples (B-13, B-14) taken in the vicinity of the BR dam, while the highest concentration of Cr (23.51.80 mg kg⁻¹) and Cd (11.50 mg kg⁻¹) - in samples

(M-13, M-14) taken from the MR. Maximum concentrations of Ni in both reservoirs were comparable, reaching: 31.15 mg kg⁻¹-BR and 27.46 mg kg⁻¹-MR, respectively (Table 3). The analysis of CV coefficient values shows that the concentration of individual trace elements in the BR sediments is much more diverse than in the MR. Calculated CV values range from 35% (Cr) to 57% (Cu). In the case of the MR, CV values range from 11% (Cu) to 33% (Cr). Certainly, the discharge of contaminated stormwater has an influence on the differences in individual HM content in the BR sediments. Suspensions and stormwater from transportation routes, parking lots and built-up areas contain Zn, Cu, Mn and Pb [32-34]. The spatial distribution of HM content in the sediments from the analyzed reservoirs is shown in Fig. 3. Analysis of the illustration confirms different spatial distribution of the studied trace elements in both reservoirs. In general, HM content increases



Fig. 3. Spatial distribution of HMs in sediments.

in flow direction for the MR. Whereas, in the BR, apart from increasing HM content while approaching the dam, there is an obvious change in HM concentration along the transverse axis of the reservoir Fig. 3.

While comparing content of the studied HMs in sediments of both reservoirs with the value of geochemical background for alluvia and water sediments in Poland [25], we observe that in all analyzed samples for Cr, Ni, Cu and Pb (BR), as well as Cr, Cu and Cd (MR), it was larger than the boundary value. The degree of contamination with Cd in the MR sediments can be particularly distinguished, compared with other analyzed trace elements. The mean content of this metal in sediments is more than seventeen times higher than the background value. This situation shall be considered threatening for the environment due to the strong toxic properties of this element. Mean Pb content in the BR sediments was more than six times higher than the background value, while Cr, Ni and Cu: between 2.1 and 3.9 times higher. Considerable content of Cr, Ni, Cu and Pb in the BR sediments, as well as Cr, Cu and Cd in the MR sediments may prove anthropogenic origins of these elements. As already mentioned before, anthropogenic HM sources in the BR include stormwater and, to a lesser extent, municipal effluents (no sanitary sewage system). Whereas, in the case of the MR, agriculture and livestock farming activity constitute the anthropogenic sources of HM. The intense agricultural activity requires considerable volumes of mineral fertilizers, which contain HMs, including Cd [35-37]. The small mean of Cd content in the BR, and Zn, Ni and Pb in the MR, under or slightly over the geochemical background value (Table 3) proves the geogenic origins of these metals.

4.2. Pearson correlation and PCA analysis

The occurrence of strong correlation connections in the content of individual HMs in bottom sediments proves the existence of many geochemical relations among them [28,37]. It also provides valuable information regarding the sources of their origin. It is usually assumed that a positive value of the correlation coefficient among HMs indicates their common source and much the same behavior during transport [12,19]. Completed analysis prove that there is a strong

(Table 4), statistically significant, positive correlation connection among Zn, Pb and Cu in the BR. This indicates a common source of these elements and much the same behavior during transport [19,38]. A strong positive connection was also observed between Cr and Ni. However, PCA analysis shows that the sources these metals originate from are different (groups A and B, Fig. 4), and different factors determine their spatial distribution in the BR reservoir. Diagram 4 shows that two factors (PC 1 and PC 2) have a substantial effect on HM concentration in the BR sediments. The first factor (hydromorphological) covers more than 52% of the total variance, while PC 2 (stormwater) - more than 29%. PC 1 is strongly negatively correlated with Cr, Ni and Si, TOM, LI Fig. 4. This means that hydrodynamic factors determining sediment grading in a reservoir and organic matter movements affect Cr and Ni distribution. Probably, in the majority these metals enter the BR with water of the Kamienna River, and they may have geogenic character. A strongly positive connection between Zn, Pb, Cu and PC 2, as well as higher concentration of these elements in sediments, confirm their anthropogenic origins.

Strong positive connections among Pb and Ni, as well as Cu, Cr and Cd were observed in the MR. According to the authors, the low content of Pb and Ni in sediments proves their geogenic origins. Whereas, considerable Cd content connected with Cr and Cu confirms the view presented here as regards their relationship with agriculture and livestock farming within the reservoir basin. The PCA analysis shows that the studied HMs (except Zn) are negatively correlated with PC 1, which covers more than 64% of the total variance. Moreover, same as in the BR, the TOM, Si and LI are negatively correlated with PC 1, which confirms the idea of a significant impact of hydrodynamic flow conditions on the spatial distribution of HMs within a reservoir.

4.3. Degree of bottom sediments pollution with HMs and ecological risk assessment

The potential impact of HM on the aquatic ecosystem can be assessed using TEL and PEL indices. If the content of an analyzed element in bottom sediments is smaller than TEL value, no adverse effect on aquatic biota is observed. In case

Table 4 Value of Pearson correlation coefficient between selected indicators

Correlation	Cr	Zn	Ni	Cu	Pb	Cd	Si	TOM	PERI	TRI
Cr		-0.066	0.381	0.790*	0.406	0.736*	0.661*	0.729*	0.824*	0.774*
Zn	0.247		-0.107	-0.056	0.076	-0.313	-0.210	-0.149	-0.197	-0.248
Ni	0.822*	-0.006		0.335	0.664*	0.437	0.759*	0.474	0.588*	0.487
Cu	0.389	0.704*	0.107		0.257	0.802*	0.518*	0.691*	0.834*	0.820*
Pb	0.304	0.914*	-0.045	0.814*		0.371	0.579*	0.202	0.573*	0.443
Cd	-0.218	0.621*	-0.306	0.436	0.611*		0.637*	0.709*	0.959*	0.994*
Si	0.685*	-0.459	0.402	0.121	-0.263	-0.393		0.693*	0.742*	0.674*
TOM	0.860*	0.132	0.539*	0.419	0.306	-0.299	0.866*		0.728*	0.722*
PERI	0.649*	0.804*	0.405	0.885*	0.873	0.413	0.189	0.545*		0.981*
TRI	0.557*	0.892*	0.318	0.841*	0.918	0.540*	0.068	0.426	0.980*	

* – correlation significant at the 0.05 level, 0.247 – Bliżyn Reservoir , 0.247 – Małoszówka Reservoir



Fig. 4. Results of PCA analysis; (a) Bliżyn Reservoir and (b) Małoszówka Reservoir.

if that content exceeds PEL value, the adverse HM effect on aquatic biota is frequently observed. According to the above criterion, only Pb content in the BR sediments exceeds PEL value (samples B1, B13 and B14 taken in the vicinity of left shore and dam of the reservoir - 21% of the analyzed samples), which proves the adverse effect of this HM on aquatic biota. In the remaining samples (71% of all determinations) from the BZ, Pb content was higher than TEL value and at the same time, it was less than PEL. The same was observed for Zn (50% of samples), Ni (57% of samples) and Cu (14% of samples), confirming the occasional yet adverse effect of stormwater discharge on the water ecosystem in the reservoir. Cr, Zn, Ni, Cu and Pb content in the MR sediments do not exceed TEL value, and thus these HMs have no adverse effect on aquatic biota. At the same time, in the case of Cd, PEL values were exceeded in all examined samples from 1.6 to 3.1 times, proving frequent occurrence of an adverse effect of this HM on aquatic biota.

PERI and TRI indices were used to assess the toxicity risk of HMs in the bottom sediments of the studied reservoirs. The PERI value below 150 indicates low ecological risk potential [22,38]. According to this criterion, the BR and MR bottom sediments are characterized by the low and moderate potential of risk related to the concentrations of the analyzed HMs. The calculated PERI values ranged within 17.91–56.12 in the BR, and 123.83–237.33.25 in the MR (Table 5, Fig. 5). Whereas, the TRI index values ranged from 1.85 to 6.11 (BR) and from 7.95 to 15.00 (MR) (Table 5, Fig. 5). In general, values smaller than 5 appeared in 11 out of 14 sample-taking locations in the BR. The TRI values ranging from 5 to 10 were observed in four cases only (B-1, B-7, B-13 and B14) - indicating low ecological risk. Pb and Zn concentrations showed the highest share in the TRI index, 33% and 18% on average. Definitely higher TRI values were observed for the MR. TRI values between 5 and 10 appeared only once (M-1). However, values ranging between 10 and 15 were observed fourteen times (more than 93% of all examined sediment samples from this reservoir)-indicating moderate

Table 5Results of statistical analysis for PERI and TRI

Parameter	PERI	TRI	PERI	TRI
	Bliżyn Reservoir		Małoszówka Reservoir	1
Maximum	56.12	6.11	237.33	15.00
Minimum	17.91	1.85	123.83	7.95
Mean	35.46	3.99	189.25	12.10
Median	33.40	3.71	199.50	12.66
CV %	33	33	15	15
SD	11.58	1.32	29.32	1.79
R^2	0.96		0.96	

 R^2 is the coefficient of determination.

ecological risk. The Cd concentration had the highest share in the TRI index, over 86% on average.

Calculated values of the coefficient of determination between PERI and TRI indices ($R^2 = 0.96$) prove their high correlation. This point that both factors are characterized by similar results and can be used alternately with respect to the assessment of bottom sediments quality [37,38].

5. Conclusions

Obtained results of completed analysis allow making the following conclusions:

- The content of heavy metals in bottom sediments is an individual characteristic of each water reservoir, determined by many interconnected natural and anthropogenic factors.
- Sediments accumulating in the vicinity of dams of both analyzed reservoirs were most polluted with HM. PEL threshold value was exceeded in case of Pb content for



Fig. 5. Classified spatial distribution of PERI and TRI of bottom sediments.

BR., and Cd – for MR., showing an adverse effect of these HMs on aquatic biota.

- PERI values suggested that bottom sediments in BR exhibited low ecological risk, while MR exhibited moderate ecological risk from metal pollution. The TRI value suggested that 28% of the sediment sampling sites in BR exhibited low toxic risk and more than 93% of the sediment sampling sites in MR exhibited moderate toxic risk. Based on the performed evaluation, we can state that Pb (BR) and Cd (MR) in the sediment samples were the main cause of the adverse biological effects.
- The key factors determining the spatial distribution of HM in the bowls of the analyzed reservoirs are reservoir morphology and hydrodynamic conditions of water flow. These factors affect the grain composition of sediments (sediment grading) and organic matter content. Cr and Ni content in the BR sediments and Cr, Cu, Cd content in the MR sediments was strongly, statistically significantly connected with the TOM content. Whereas, human activity may have a significant, direct influence on the form and character of regression connections between HMs and physical properties of sediments.

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References

- Ł. Bąk, Silting and Bottom Sediments of Small Water Reservoirs in the Kielce Upland, Wydawnictwo Politechniki Świętokrzyskiej, Kielce, 2017 (in Polish).
- [2] D.D. MacDonald, C.G. Ingersoll, T.A. Berger, Development and evaluation of consensus-based sediment quality guidelines

for freshwater ecosystems, Arch. Environ. Contam. Toxicol., 39 (2000) 20-31.

- [3] E. Szalińska, Sediment Role in Assessment of Freshwater Environment Quality, Wydawnictwo Politechniki Krakowskiej, Kraków, 2011 (in Polish).
- [4] Y. Wang, L. Yang, L. Kong, E. Liu, L. Wang, J. Zhu, Spatial distribution, ecological risk assessment and source identification for heavy metals in surface sediments from Dongping Lake, Shandong, East China, Catena, 125 (2015) 200–205.
- [5] N. Ekere, N. Yakubu, J. Ihedioha, Ecological risk assessment of heavy metals and polycyclic aromatic hydrocarbons in sediments of rivers Niger and Benue confluence, Lokoja, Central Nigeria, Environ. Sci. Pollut. Res., 24 (2017) 18966–18978.
- [6] J. Latosińska, The influence of temperature and time of sewage sludge incineration on the mobility of heavy metals, Environ. Prot. Eng., 44 (2017) 105–122.
- [7] E. Ansah, D. Nukpezah, J.N. Hogarh, Levels and distribution of heavy metals in Weija reservoir, Accra, Ghana, West Afr. J. Appl. Ecol., 26 (2018) 74–88.
- [8] E.L. Enserink, J.L. Maas-Diepeveen, C.J. Van Leeuwen, Combined effects of metals: an ecotoxicological evaluation, Water Res., 25 (1991) 679–687.
- [9] J. Li, H. Dong, D. Zhang, B. Han, C. Zhu, S. Liu, X. Liu, Q. Ma, X. Li, Sources and ecological risk assessment of PAHs in surface sediments from Bohai Sea and northern part of the Yellow Sea, China, Mar. Pollut. Bull., 69 (2015) 485–490.
- [10] A. Sałata, Ł. Bąk, L. Dąbek, E. Ozimina, Assessment of the degree of pollution of sediments from the rainstorm sewer system in the urbanized catchment, Desal. Wat. Treat., 57 (2016) 1478–1489.
- [11] J. Górski, Ł. Bąk, A. Sałata, K. Górska, A. Rabajczyk, Changes of heavy metal concentration in rainfall wastewater in urban catchment, Desal. Wat. Treat., 117 (2018) 257–266.
- [12] P. Gierszewski, Heavy metals concentration in sediments of Włocławek reservoir as an indicator of hydrodynamic conditions of deposition, Landform Analysis, 9 (2008) 79–82.
- [13] M. Sojka, J. Jaskuła, M. Siepak, Heavy metals in bottom sediments of reservoirs in the lowland area of western Poland: concentrations, distribution, sources and ecological risk, Water, 11 (2019) 1–20.
- [14] N. de Castro-Catalí, M. Kuzmanovic, N. Roig, J. Sierra, A. Ginebreda, D. Barceló, S. Pérez, M. Petrovic, Y. Picóh, M. Schuhmacher, I. Muñoz, Ecotoxicity of sediments in rivers:

invertebrate community, toxicity bioassays and toxic unit approach as complementary assessment tools, Sci. Total Environ., 540 (2016) 297–306.

- [15] D. Ciszewski, T.M. Grygar, A review of flood-related storage and remobilization of heavy metal pollutants in river systems, Water Air Soil Pollut., 227 (2016) 227–239.
- [16] F. Frémion, F. Bordas, B. Mourier, J.F. Lenain, T. Kestens, A. Courtin-Nomade, Influence of dams on sediment continuity: a study case of a natural metallic contamination, Sci. Total Environ., 547 (2016) 282–294.
- [17] H.I. Farhat, W. Aly, Effect of site on sedimentological characteristics and metal pollution in two semi-enclosed embayments of great freshwater reservoir: Lake Nasser, Egypt, J. Afr. Earth Sci., 141 (2018) 194–206.
- [18] H. Smal, S. Ligeza, A. Wójcikowska-Kapusta, S. Baran, D. Urban, R. Obroślak, A. Pawłowski, Spatial distribution and risk assessment of heavy metals in bottom sediments of two small dam reservoirs (south-east Poland), Arch. Environ. Prot., 41 (2015) 67–80.
- [19] A. Baran, M. Tarnawski, T. Koniarz, Spatial distribution of trace elements and ecotoxicity of bottom sediments in Rybnik reservoir, Silesian-Poland, Environ. Sci. Pollut. Res., 23 (2016) 17255–17268.
- [20] PN-EN ISO 11885:2009, Water Quality-Determination of Selected Elements using Optical Emission Spectrometry with Inductively Coupled Plasma (ICP-OES), Available at: https:// www.pkn.pl/en.
- [21] A. Ostrowska, S. Gawliński, Z. Szczubiałka, Methods of Analysis and Assessment of Soil and Plant Properties, Environmental Protection Institute, Warsaw, 1991.
- [22] L. Hakanson, An ecological risk index for aquatic pollution control. A sedimentological approach, Water Res., 14 (1980) 975–1001.
- [23] G. Zhang, J. Bai, Q. Zhao, Q. Lu, J. Jia, X. Wen, Heavy metals in wetland soils along a wetland-forming chronosequence in the Yellow River Delta of China: Levels, sources and toxic risks, Ecol. Indic., 69 (2016) 331–339.
- [24] S.B. Fang, X.B. Jia, X.Y. Yang, Y.D. Li, S.Q. An, A method of identifying priority spatial patterns for management of potential ecological risks posed by heavy metals, J. Hazard. Mater., 237–238 (2012) 290–298.
- [25] I. Bojakowska, G. Sokołowska, Geochemical class of purity of water sediments, Przegl Geol., 46 (1998) 49–54 (in Polish).
- [26] D.D. Macdonald, C.G. Ingersoll, T.A. Berger, Development and evaluation of consensus-based sediment quality guidelines for freshwater ecosystems, Arch. Environ. Contam. Toxicol., 39 (2000) 20–31.

- [27] N. El-Shejmy, C. Valeo, A. Habib, Digital Terrain Modeling: Acquisition, Manipulation and Applications, Norwood Artech House, 2005.
- [28] A. Sałata, Ł. Bąk, K. Chmielowski, A. Rabajczyk, Metal pollution of sediments in small water reservoirs in the Kielce Highland (South-Eastern Poland), Arch. Environ. Prot., 45 (2019) 12–21.
- [29] R.W. Duck, J. McManus, Sediment yields in lowland Scotland derived from reservoir surveys. Transactions of the Royal Society of Edinburgh, Earth Sciences, 78 (1987) 369–377.
- [30] G. Verstraeten, J. Poesen, Variability of dry sediment bulk density between and within retention ponds and its impact on the calculation of sediment yields, Earth Surf. Processes Landforms, 26 (2001) 375–394.
- [31] B. Michalec, Appraisal of silting intensity of small water reservoirs in the Upper Vistula river basin, Wydawnictwo Uniwersytetu Rolniczego w Krakowie, Kraków, 2008 (in Polish).
- [32] H. Gan, M. Zhuo, D. Li, Y. Zhou, Quality characterization and impact assessment of highway runoff in an urban and rural area of Guangzhou, China, Environ. Monit. Assess., 140 (2008) 147–159.
- [33] Ł. Bąk, J. Górski, K. Górska, B. Szeląg, Solids and heavy metals content of selected rainwater waves in an urban catchment area: a case study, Ochr Sr., 34 (2012) 49–52 (in Polish).
- [34] D. Wicke, T.A. Cochrane, A.D. O'Sullivan, Atmospheric deposition and storm induced runoff of heavy metals from different impermeable urban surfaces, J. Environ. Monit., 14 (2012) 209–219.
- [35] K. Szydłowski, K. Rawicki, P. Burczyk, The content of heavy metals in bottom sediments of the watercourse in agricultural catchment on the example of the river Gowienica, Ecol. Eng., 18 (2017) 218–224.
- [36] J. Podlasińska, K. Szydłowski, Assessment of heavy metal pollution in bottom sediments of small water reservoirs with different catchment management, Infrastruct. Ecol. Rural Areas, 1 (2017) 987–997.
- [37] K. Rozpondek, R. Rozpondek, Evaluation of quality of bottom sediments of water reservoir Poraj by applying sediment quality guidelines and spatial analysis, ACEE J., 2 (2018) 141–147.
 [38] W. Guo, X. Liu, Z. Liu, G. Li, Pollution and potential ecological
- [38] W. Guo, X. Liu, Z. Liu, G. Li, Pollution and potential ecological risk evaluation of heavy metals in the sediments around Dongjiang Harbor, Tianjin, Procedia Environ. Sci., 2 (2010) 729–736.